



Estimating Potential for Occurrence of DNAPL at Superfund Sites

Office of Emergency and Remedial Response
Hazardous Site Control Division (OS-220W)

Quick Reference Fact Sheet

GOALS

The presence of Dense Nonaqueous Phase Liquids (DNAPL) in soils and aquifers can control the ultimate success or failure of remediation at a hazardous waste site. Because of the complex nature of DNAPL transport and fate, however, DNAPL may often be undetected by direct methods, leading to incomplete site assessments and inadequate remedial designs. Sites affected by DNAPL may require a different "paradigm," or conceptual framework, to develop effective characterization and remedial actions (2).

To help site personnel determine if DNAPL-based characterization strategies should be employed at a particular site, a guide for estimating the potential for DNAPL occurrence was developed. The approach, described in this fact sheet, requires application of two types of existing site information:

- Historical Site Use Information
- Site Characterization Data

By using available data, site decision makers can enter a system of two flowcharts and a classification matrix for estimating the potential for DNAPL occurrence at a site. If the potential for DNAPL occurrence is low, then conventional site assessment and remedial actions may be sufficient. If the potential for DNAPL is moderate or high, however, a different conceptual approach may be required to account for problems associated with DNAPL in the subsurface.

BACKGROUND

DNAPLs are separate-phase hydrocarbon liquids that are denser than water, such as chlorinated solvents (either as a single component or as mixtures of solvents), wood preservative wastes, coal tar wastes, and pesticides. Until recently, standard operating practice in a variety of industries resulted in the release of large quantities of DNAPL to the subsurface. Most DNAPLs undergo only limited degradation in the subsurface, and persist for long periods while slowly releasing soluble organic constituents to ground water through dissolution. Even with a moderate DNAPL release, dissolution may continue for hundreds of years or longer under natural conditions before all the DNAPL is dissipated and concentrations of soluble organics in ground water return to background levels.

DNAPL exists in the soil/aquifer matrix as free-phase DNAPL and residual DNAPL. When released at the surface, free-phase DNAPL moves downward through the soil matrix under the force of gravity or laterally along the surface of sloping fine-grained stratigraphic units. As the free-phase DNAPL moves, blobs or ganglia are trapped in pores and/or fractures by capillary forces (7). The amount of the trapped DNAPL, known as residual saturation, is a function of the physical properties of the DNAPL and the hydrogeologic characteristics of the soil/aquifer medium and typically ranges from 5% to 50% of total pore volume. At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Once in the subsurface, it is difficult or impossible to recover all of the trapped residual DNAPL. The conventional aquifer remediation approach, ground water pump-and-treat, usually removes only a small fraction of trapped residual DNAPL (11, 21, 26). Although many DNAPL removal technologies are currently being tested, to date there have been no field demonstrations where sufficient DNAPL has been successfully recovered from the subsurface to return the aquifer to drinking water quality. The DNAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to ground water, preventing the restoration of DNAPL-affected aquifers for many years.



DNAPL TRANSPORT AND FATE - CONCEPTUAL APPROACHES

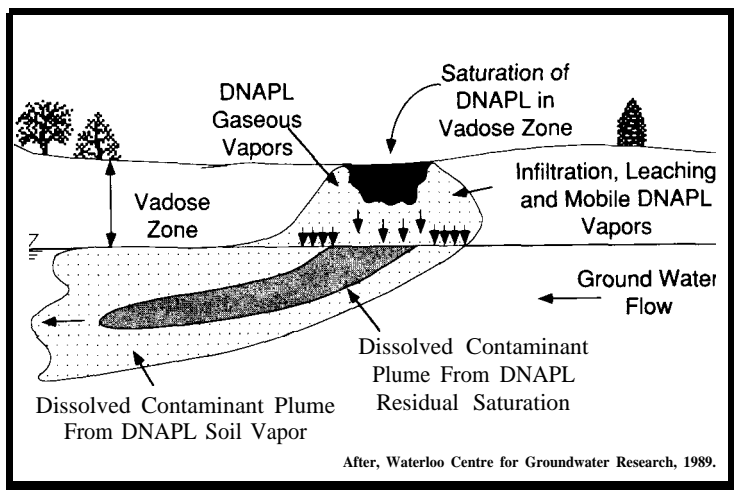
The major factors controlling DNAPL migration in the subsurface include the following (5):

- the volume of DNAPL released;
- the area of infiltration at the DNAPL entry point to the subsurface;
- the duration of release;
- properties of the DNAPL, such as density, viscosity, and interfacial tension;
- properties of the soil/aquifer media, such as pore size and permeability;
- general stratigraphy, such as the location and topography of low-permeability units;
- micro-stratigraphic features, such as root holes, small fractures, and slickensides found in silt/clay layers.

To describe the general transport and fate properties of DNAPL in the subsurface, a series of conceptual models (24) are presented in the following figures:

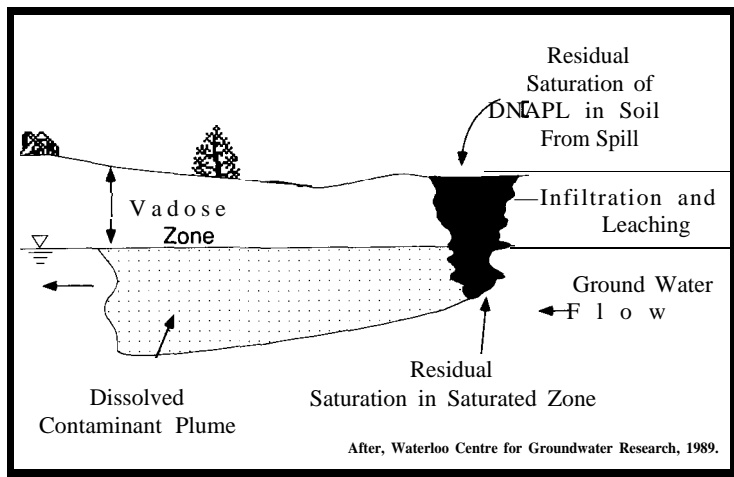
Case 1: DNAPL Release to Vadose Zone Only

After release on the surface, DNAPL moves vertically downward under the force of gravity and soil capillarity. Because only a small amount of DNAPL was released, all of the mobile DNAPL is eventually trapped in pores and fractures in the unsaturated zone. Infiltration through the DNAPL zone dissolves some of the soluble organic constituents in the DNAPL, carrying organics to the water table and forming a dissolved organic plume in the aquifer. Migration of gaseous vapors can also act as a source of dissolved organics to ground water (13).



Case 2: DNAPL Release to Unsaturated and Saturated Zones

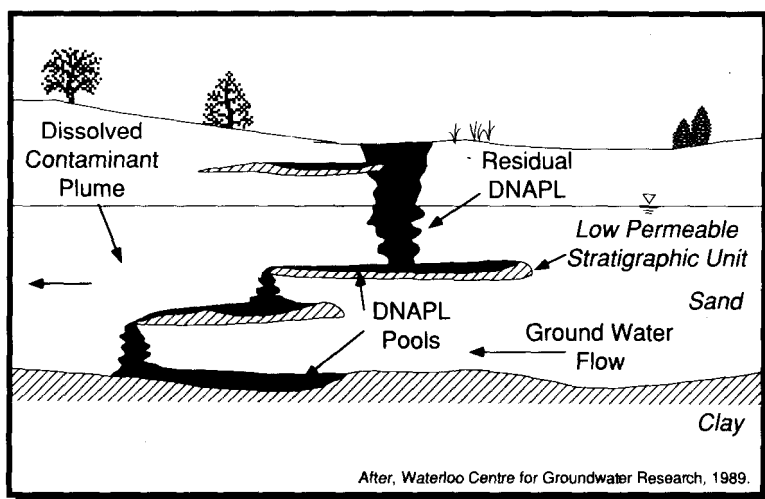
If enough DNAPL is released at the surface, it can migrate all the way through the unsaturated zone and reach a water-bearing unit. Because the specific gravity of DNAPL is greater than water, it continues downward until the mobile DNAPL is exhausted and is trapped as a residual hydrocarbon in the porous media. Ground water flowing past the trapped residual DNAPL dissolves soluble components of the DNAPL, forming a dissolved plume downgradient of the DNAPL zone. As with Case 1, water infiltrating down from the source zone also carries dissolved constituents to the aquifer and contributes further to the dissolved plume.



CONCEPTUAL APPROACHES - Continued

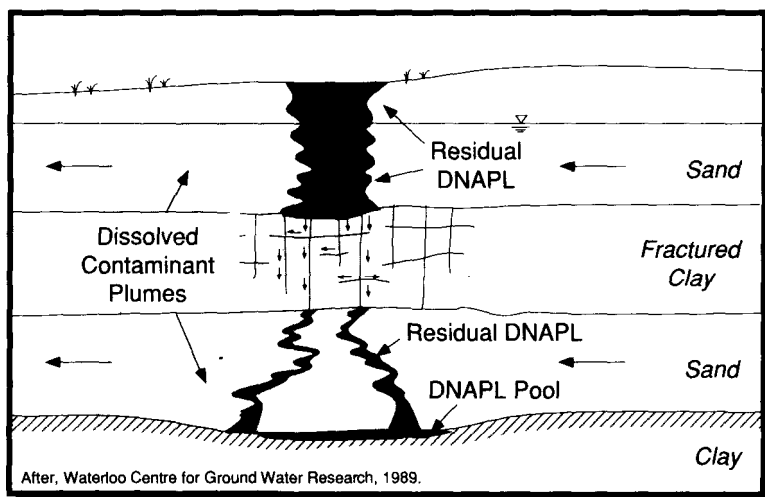
Case 3: DNAPL Pools and Effect of Low-Permeability Units

Mobile DNAPL will continue vertical migration until it is trapped as a residual hydrocarbon (Case 1 and Case 2) or until low-permeability stratigraphic units are encountered which create DNAPL "pools" in the soil/aquifer matrix. In this figure, a perched DNAPL pool fills up and then spills over the lip of the low-permeability stratigraphic unit. The spill-over point (or points) can be some distance away from the original source, greatly complicating the process of tracking the DNAPL migration.



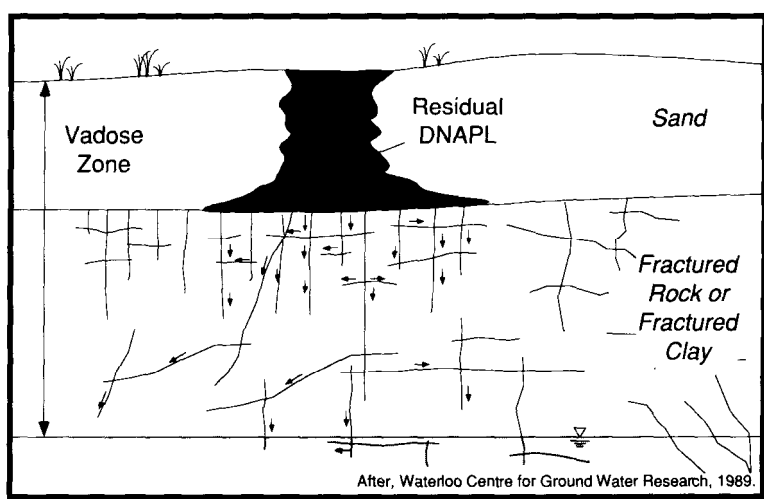
Case 4: Composite Site

In this case, mobile DNAPL migrates vertically downward through the unsaturated zone and the first saturated zone, producing a dissolved constituent plume in the upper aquifer. Although a DNAPL pool is formed on the fractured clay unit, the fractures are large enough to permit vertical migration downward to the deeper aquifer (see Case 5, below). DNAPL pools in a topographic low in the underlying impermeable unit and a second dissolved constituent plume is formed.

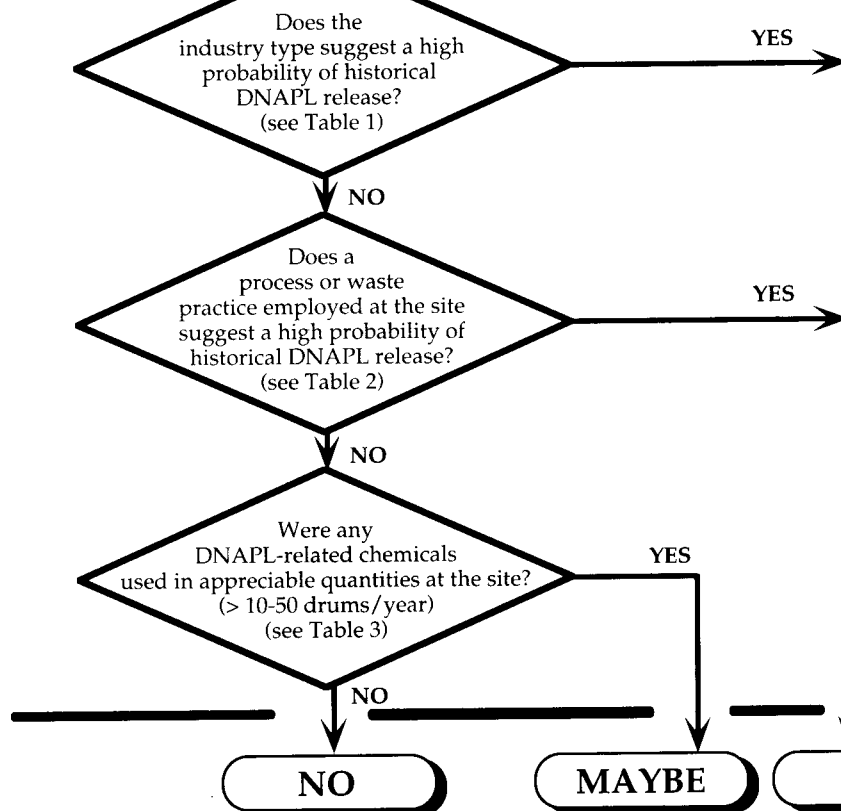


Case 5: Fractured Rock or Fractured Clay System

DNAPL introduced into a fractured rock or fractured clay system follows a complex pathway based on the distribution of fractures in the original matrix. The number, density, size, and direction of the fractures usually cannot be determined due to the extreme heterogeneity of a fractured system and the lack of economical aquifer characterization technologies. Relatively small volumes of DNAPL can penetrate deeply into fractured systems due to the low retention capacity of the fractures and the ability of some DNAPLs to migrate through very small (< 20 microns) fractures. Many clay units, once considered to be relatively impermeable to DNAPL migration, often act as fractured media with preferential pathways for vertical and horizontal DNAPL migration.



Does Historical Site Use Information Indicate Presence of DNAPL?



INSTRUCTIONS

1. Answer questions in Flowchart 1 (historical site use info. - page 4).
2. Answer questions in Flowchart 2 (site characterization data - page 5).
3. Use "Yes," "No," and "Maybe" answers from both flowcharts and enter Occurrence of DNAPL matrix (page 6).

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TABLE 1

Industries with high probability of historical DNAPL release:

- Wood preservation (creosote)
- Old coal gas plants (mid-1800s to mid-1900s)
- Electronics manufacturing
- Solvent production
- Pesticide manufacturing
- Herbicide manufacturing
- Airplane maintenance
- Commercial dry cleaning
- Instrument manufacturing
- Transformer oil production
- Transformer reprocessing
- Steel industry coking operations (coal tar)
- Pipeline compressor stations

TABLE 2

Industrial processes or waste disposal practices with high probability of historical DNAPL release:

- Metal cleaning/decreasing
- Metal machining
- Tool-and-die operations
- Paint removing/stripping
- Storage of solvents in underground storage tanks
- Storage of drummed solvents in uncontained storage areas
- Solvent loading and unloading
- Disposal of mixed chemical wastes in landfills
- Treatment of mixed chemical wastes in lagoons or ponds

TABLE 3 DNAPL-Related Chemicals (20):

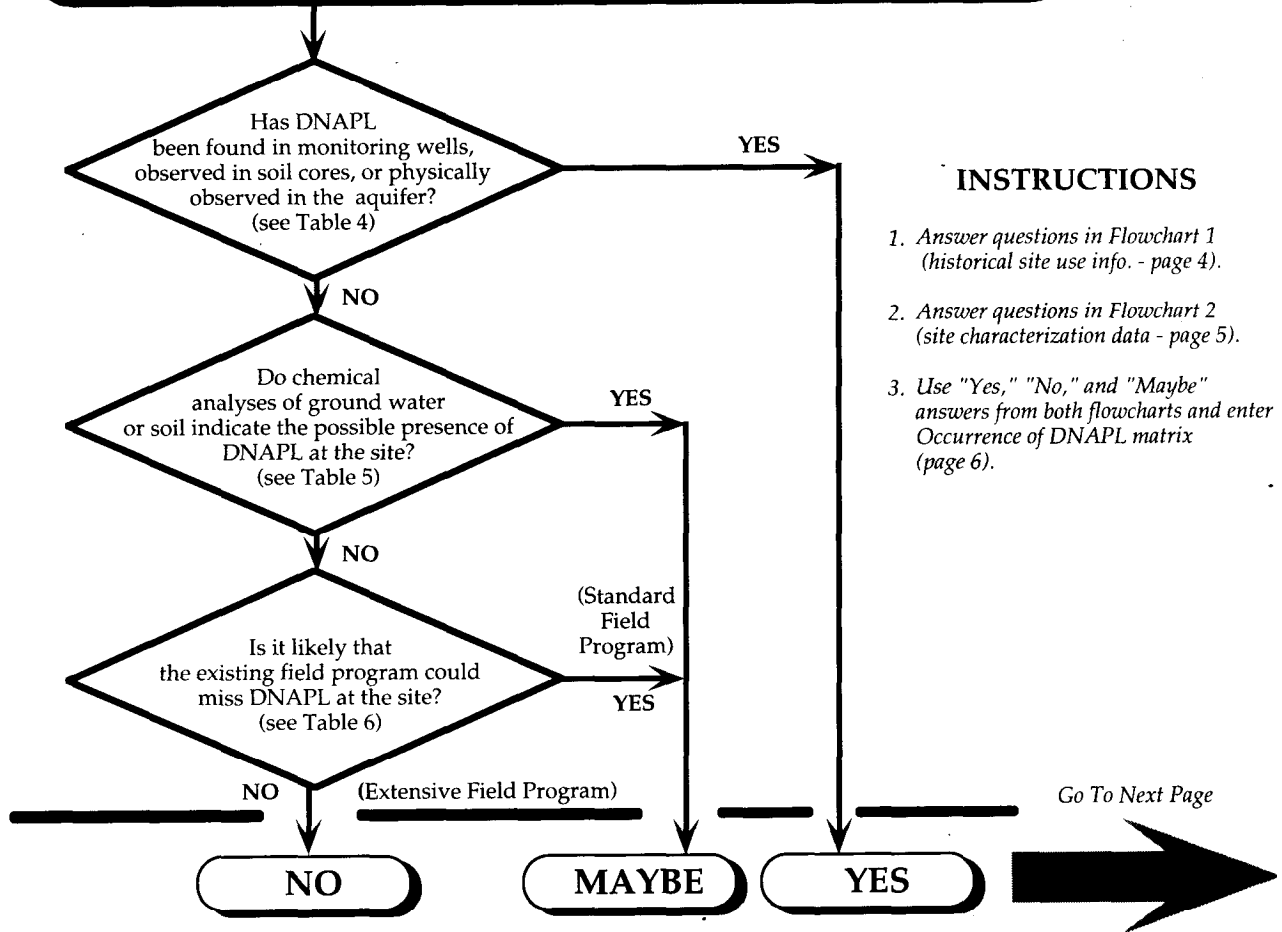
Halogenated Volatiles	Non-Halogenated Semi-Volatiles
Chlorobenzene	2-Methyl Naphthalene
1,2-Dichloropropane	o-Cresol
1,1-Dichloroethane	p-Cresol
1,2-Dichloroethylene	2,4-Dimethylphenol
Trans-1,2-Dichloroethylene	m-Cresol
Cis-1,2-Dichloroethylene	Phenol
1,1,1-Trichloroethane	Naphthalene
Methylene Chloride	Benzo(a)Anthracene
1,1,2-Trichloroethane	Fluorene
Trichloroethylene	Acenaphthene
Chloroform	Anthracene
Carbon Tetrachloride	Dibenzo(a,h)Anthracene
1,1,2,2-Tetrachloroethane	Fluoranthene
Tetrachloroethylene	Pyrene
Ethylene Dibromide	Chrysene
	2,4-Dinitrophenol
Halogenated Semi-Volatiles	Miscellaneous
1,4-Dichlorobenzene	Coal Tar
1,2-Dichlorobenzene	Creosote
Aroclor 1242, 1254, 1260	
Chlordane	
Dieldrin	
2,3,4,6-Tetrachlorophenol	
Pentachlorophenol	

Note:

The potential for DNAPL release increases with the size and active period of operation for a facility, industrial process, or waste disposal practice.

Note: Many of these chemicals are found mixed with other chemicals or carrier oils.

Do Site Characterization Data Indicate Presence of DNAPL?



INSTRUCTIONS

1. Answer questions in Flowchart 1 (historical site use info. - page 4).
2. Answer questions in Flowchart 2 (site characterization data - page 5).
3. Use "Yes," "No," and "Maybe" answers from both flowcharts and enter Occurrence of DNAPL matrix (page 6).

TABLE 4

Methods to confirm DNAPL in wells:

- NAPL/water interface probes that signal a change in conductivity of the borehole fluid
- Weighted cotton string lowered down well
- Pumping and inspecting recovered fluid
- Transparent bottom-loading bailers
- Mechanical discrete-depth samplers.

In general, the depth of DNAPL accumulation does not provide quantitative information regarding the amount of DNAPL present (24).

Methods to confirm DNAPL in soil samples

Visual examination of cores or cuttings may not be effective for confirming the presence of DNAPL except in cases of gross DNAPL contamination. Methods for enhancing visual inspection of soil samples for DNAPL include:

- Shaking soil samples in a jar with water to separate the DNAPL from the soil (14).
- Performing a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases (20).

TABLE 5

Conditions that indicate potential for DNAPL at site based on laboratory data:

Condition 1:

Concentrations of DNAPL-related chemicals (see pg. 3) in ground water are > 1% of pure phase volubility or effective volubility, (defined in Worksheet 1, pg. 7) (25).

Condition 2:

Concentrations of DNAPL-related chemicals on soils are > 10,000 mg/kg (equal to 1 % of soil mass) (6).

Condition 3:

Concentrations of DNAPL-related chemicals in ground water calculated from water/soil partitioning relationships and soil samples are > pure phase volubility or effective solubility (see Worksheet 2, pg. 7).

Condition 4

Concentrations of DNAPL-related chemicals in ground water **increase** with depth or appear in **anomalous** up gradient / across gradient locations (25).

TABLE 6

Characteristics of extensive field programs that can help indicate the presence or absence of DNAPL (if several are present, select "NO"):

- Numerous monitoring wells, with wells screened in topographic lows on the surface of fine-grained, relatively impermeable units.
- Multi-level sampling capability.
- Numerous organic chemical analyses of soil samples at different depths using GC or GC/MS methods.
- Well-defined site stratigraphy, using numerous soil borings, a cone penetrometer survey, or geophysics.
- Data from pilot tests or "early action" projects that indicate the site responds as predicted by conventional solute transport relationships, rather than responding as if additional sources of dissolved contaminants are present in the aquifer (11, 25).

Note: This procedure is designed primarily for hydrogeologic settings comprised of gravel, sand, silt, or clay and may not be applicable to karst or fractured rock settings.

Potential for Occurrence of DNAPL at Superfund Sites

DNAPL Category

		Do Characterization Data Indicate Presence of DNAPL? (Chart 2)		
		Yes	Maybe	No
Does Historical Use Indicate Presence of DNAPL? (Chart 1)	Yes	I	I - II	II
	Maybe	I	II	II - III
	No	I	II	III

Category

Implications for Site Assessment

**high potential
for DNAPL
at site.**



- The risk of spreading contaminants increases with the proximity to a potential DNAPL zone. Special precautions should be taken to ensure that drilling does not create pathways for continued vertical migration of free-phase DNAPLs. In DNAPL zones, drilling should be suspended when a low-permeability unit or DNAPL is first encountered. Wells should be installed with short screens (< 10 feet). If required, deeper drilling through known DNAPL zones should be conducted only by using double or triple-cased wells to prevent downward migration of DNAPL. As some DNAPLs can penetrate fractures as narrow as 10 microns, special care must be taken during all grouting, cementing, and well sealing activities conducted in DNAPL zones.
- In some hydrogeologic settings, such as fractured crystalline rock, it is impossible to drill through DNAPL with existing technology without causing vertical migration of the DNAPL down the borehole, even when double or triple casing is employed (2).
- The subsurface DNAPL distribution is difficult to delineate accurately at some sites. DNAPL migrates preferentially through selected pathways (fractures, sand layers, etc.) and is affected by small-scale changes in the stratigraphy of an aquifer. Therefore, the ultimate path taken by DNAPL can be very difficult to characterize and predict.
- In most cases, fine-grained aquitards (such as clay or silt units) should be assumed to permit downward migration of DNAPL through fractures unless proven otherwise in the field. At some sites it can be exceptionally difficult to prove otherwise even with intensive site investigations (2).
- Drilling in areas known to be DNAPL-free should be performed before drilling in DNAPL zones in order to form a reliable conceptual model of site hydrogeology, stratigraphy, and potential DNAPL pathways. In areas where it is difficult to form a reliable conceptual model, an "outside-in" strategy may be appropriate: drilling in DNAPL zones is avoided or minimized in favor of delineating the outside dissolved-phase plume (2). Many fractured rock settings may require this approach to avoid opening further pathways for DNAPL migration during site-assessment.

[I Moderate
potential for
DNAPL at site.

- 1 Due to the potential risk for exacerbating ground-water contamination problems during drilling through DNAPL zones, the precautions described for Category I should be considered during site assessment. Further work should focus on determining if the site is a "DNAPL site."

III Low potential
for DNAPL
at site.

- 1 DNAPL is not likely to be a problem during site characterization, and special DNAPL precautions are probably not needed. Floating free-phase organics (LNAPLs), sorption, and other factors can complicate site assessment and remediation activities, however.

Worksheet 1: Calculation of Effective Volubility (from Shiu, 1988; Feenstra, Mackay, & Cherry, 1991)

For a single-component DNAPL, the pure-phase volubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For DNAPLs comprised of a mixture of chemicals, however, the **effective volubility** concept should be employed:

$$S_i^e = X_i S_i$$

Where

S_i^e = the effective volubility (the theoretical upper-level dissolved-phase concentration of a constituent in ground water in equilibrium with a mixed DNAPL; in mg/l)

X_i = the mole fraction of component i in the DNAPL mixture (obtained from a lab analysis of a DNAPL sample or estimated from waste characterization data)

S_i = the pure-phase volubility of compound i in mg/l (usually obtained from literature sources)

For example, if a laboratory analysis indicates that the mole fraction of trichloroethylene (TCE) in DNAPL is 0.10, then the effective solubility would be 110 mg/l [pure phase solubility of TCE times mole fraction TCE: (1100 mg/l) * (0.10) = 110 mg/l]. Effective solubilities can be calculated for all components in a DNAPL mixture. Insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective volubility of more soluble organics but will not contribute dissolved-phase organics to ground water. *Please note that this relationship is approximate and does not account for non-ideal behavior of mixtures, such as co-solvency, etc.*

Worksheet 2: Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples (From Feenstra, Mackay, and Cherry, 1991)

To estimate if NAPLs are present, a partitioning calculation based on chemical and physical analyses of soil samples from **the saturated zone** (from cores, excavations, etc.) can be applied. This method tests the assumption that all of the organics in the subsurface are either dissolved in ground water or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in ground water is determined. If the theoretical pore-water concentration is greater than the estimated volubility of the organic constituent of interest, then NAPL may be present at the site. A worksheet for performing this calculation is presented below; see Feenstra, Mackay, and Cherry (1991) for the complete methodology.

Step 1: Calculate S_i^e , the effective volubility of organic constituent of interest.

See Worksheet 1, above.

Step 2: Determine **Koc**, the organic carbon-water partition coefficient from one of the following:

- A) Literature sources (such as 22) or
- B) From empirical relationships based on **Kow**, the octanol-water partition coefficient, which is also found in the literature (22). For example, **Koc** can be estimated from Kow using the following expression developed for polyaromatic hydrocarbons (8):

$$\text{Log Koc} = 1.0 * \text{Log Kow} - 0.21$$

Other empirical relationships between Koc and Kow are presented in refs. 4 and 15.

Step 3: Determine **foc**, the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for **foc** typically range from 0.03 to 0.00017 mg/mg (4). Convert values reported in percent to mg/mg.

Step 4: Determine or estimate **ρb**, the dry bulk density of the soil, from a soils analysis. Typical values range from 1.8 to 2.1 g/ml (kg/l). Determine or estimate **φw**, the water-filled porosity.

Step 5: Determine **Kd**, the partition (or distribution) coefficient between the pore water (ground water) and the soil solids:

$$Kd = Koc * foc$$

Step 6 Using **Ct**, the measured conc. of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water conc. assuming no DNAPL (i.e., C_w in mg/l):

$$C_w = \frac{(C_t * \rho_b)}{(Kd * \rho_b + \phi_w)}$$

Step 7 Compare C_w and S_i^e (from Step 1):

$$C_w > S_i^e \text{ suggests possible presence of DNAPL}$$
$$C_w < S_i^e \text{ suggests possible absence of DNAPL}$$

GLOSSARY (adapted from Cherry, 1991):

DNAPL: A Dense Nonaqueous Phase Liquid. A DNAPL can be either a single-component DNAPL (comprised of only one chemical) or a mixed DNAPL (comprised of several chemicals). DNAPL exists in the subsurface as free-phase DNAPL or as residual DNAPL (see following definitions). DNAPL does not refer to chemicals that are dissolved in groundwater.

DNAPL ENTRY LOCATION: The area where DNAPL has entered the subsurface, such as a spill location or waste pond.

DNAPL SITE: A site where DNAPL has been released and is now present in the subsurface as an immiscible phase.

DNAPL ZONE: The portion of a site affected by free-phase or residual DNAPL in the subsurface (either the unsaturated zone or saturated zone). The DNAPL zone has organics in the vapor phase (unsaturated zone), dissolved phase (both unsaturated and saturated zone), and DNAPL phase (both unsaturated and saturated zone).

DISSOLUTION: The process by which soluble organic components from DNAPL dissolve in ground water or dissolve in infiltration water and form a ground-water contaminant plume. The duration of remediation measures (either clean-up or long-term containment) is determined by 1) the rate of dissolution that can be achieved in the field, and 2) the mass of soluble components in the residual DNAPL trapped in the aquifer.

EFFECTIVE SOLUBILITY: The theoretical aqueous volatility of an organic constituent in ground water that is in chemical equilibrium with a mixed DNAPL (a DNAPL containing several organic chemicals). The effective volatility of a particular organic chemical can be estimated by multiplying its mole fraction in the DNAPL mixture by its pure phase volatility (see Worksheet 1, page 7).

FREE-PHASE DNAPL: Immiscible liquid existing in the subsurface with a positive pressure such that it can flow into a well. If not trapped in a pool, free-phase DNAPL will flow vertically through an aquifer or laterally down sloping fine-grained stratigraphic units. Also called mobile DNAPL or continuous-phase DNAPL.

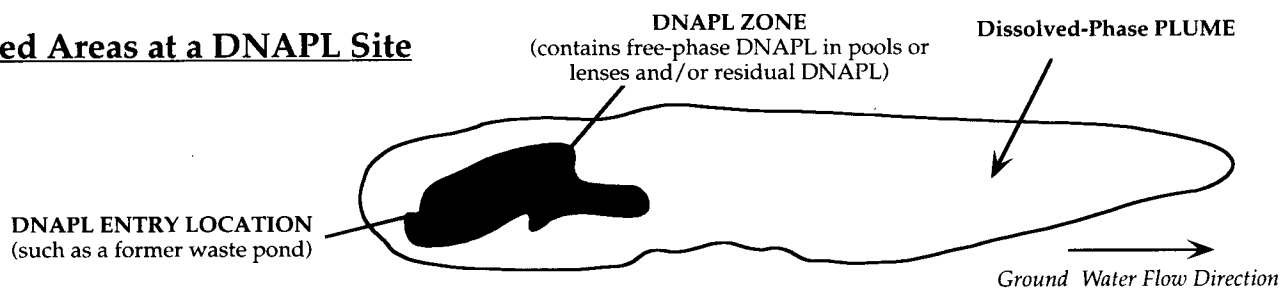
PLUME: The zone of contamination containing organics in the dissolved phase. The plume usually will originate from the DNAPL zone and extend downgradient for some distance depending on site hydrogeologic and chemical conditions. To avoid confusion, the term "DNAPL plume" should not be used to describe a DNAPL pool; "plume" should be used only to refer to dissolved-phase organics.

POOL and LENS: A pool is a zone of free-phase DNAPL at the bottom of an aquifer. A lens is a pool that rests on a fine-grained stratigraphic unit of limited areal extent. DNAPL can be recovered from a pool or lens if a well is placed in the right location.

RESIDUAL DNAPL: DNAPL held in soil pore spaces or fractures by capillary forces (negative pressure on DNAPL). Residual will remain trapped within the pores of the porous media unless the viscous forces (caused by the dynamic force of water against the DNAPL) are greater than the capillary forces holding the DNAPL in the pore. At most sites the hydraulic gradient required to mobilize all of the residual trapped in an aquifer is usually many times greater than the gradient that can be produced by wells or trenches (26).

RESIDUAL SATURATION: The saturation (the fraction of total pore space containing DNAPL) at which DNAPL becomes discontinuous and is immobilized by capillary forces (14). In unsaturated soils, residual saturation typically ranges from 5% to 20% of total pore volume, while in the saturated zone the residual saturation is higher, with typical values ranging from 15% to 50% of total pore volume (14,17). At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Defined Areas at a DNAPL Site



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